Distribution of Benzo[a]pyrene, Benzo[ghi]perylene and Some Organochlorine Compounds in Atmospheric Particulate Matter with Respect to Particle Size

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Abstract

The occurrence of some organic trace substances (PCB 101, PCB 153, p,p'-DDE, p,p'-DDT, benzo[a]pyrene (BaP), benzo[ghi]perylene(BghiP)) in different size fractions of atmospheric particulate matter was investigated. Samples were collected at the campus of the University of Bayreuth (Northern Bavaria, FRG) using a five-stage cascade impactor backed up by a glass fiber filter. Gaseous portions of the compounds were trapped by adsorption on Amberlite XAD 2. The two PAHs were in all cases solely identified on the particulate matter, while the other substances were found to partition between the particles and the vapor phase. Most of the PAHs, and the particle bound portion of p,p'-DDT was located on particles with aerodynamic diameters $\leq$ 0.45 μm. This was also the case for the PCBs, whereas considerable amounts of p,p'-DDE were found on coarser particles.

Introduction

Atmospheric transport and deposition of particle bound chemicals strongly depend on the size distribution of the particles containing these substances. While the atmospheric residence times of particles with aerodynamic diameters $\leq$ 1 μm are 100-1000 hours, they range between only 10 and 100 hours for particles with diameters of 1-10 μm *(DeWiest (1978))*.

Investigations of the distribution of pollutants with respect to particle size have focussed on heavy metals and polycyclic aromatic hydrocarbons (PAHs), usually from a toxicological perspective. Different authors concluded that PAHs are mainly associated with small particles *(Kertesz-Saringer et al. (1971), Pierce and Katz (1975), Van Vaeck et al. (1978), Müller (1984), Israel et al. (1986))*. This was also shown to be the case for many heavy metals (e.g. Pb, Cd, As) *(Natusch et al. (1974), Gladney et al. (1974), Laskus (1986), Gälli et al. (1989))*.

The size distribution of particle bound substances in the atmosphere may be due to two different mechanisms:
- *source of emission*: The particle distribution spectrum may be determined by the nature of the emission process. For instance, many compounds present in combustion gases condensate onto particle surfaces in the exhaust stream. As the particles formed in these processes generally lie between 0.08 and 2 μm (also known as the accumulation mode particle size range *(Bidleman (1988))*), one would also expect contaminants of combustion origin such as PAHs and lead in this particle size fraction.
- *partitioning due to physico-chemical properties*: Chemicals in the atmosphere can partition between the solid, vapor, and liquid phases. This partitioning is controlled by properties of the chemical and of the particulate matter (mainly surface

area and organic carbon content). According to *Müller (1984)* the organic portion of atmospheric particulate matter is concentrated nearly exclusively in the accumulation mode, which also comprises most of the surface area. For these reasons gaseous compounds are thought to sorb primarily on these particles.

In the present paper the particle size distribution of two PAHs and some organochlorine compounds was investigated.

Experimental

Sampling was performed at the campus of the University of Bayreuth, FRG (11.60°E, 50.00°N). Six 48 hours samples were collected between November 13-29,1988. The mean ambient temperatures during the sampling periods ranged from 1.8°C to -5.9°C. Particles were collected using a five-stage low pressure impactor (Berner LPI 150/0.15/3, Hauke, Gmunden, Austria) backed up by a glass fiber filter (70 mm diameter; Schleicher and Schüll no 8). Gaseous substances were adsorbed on Amberlite XAD 2 in traps connected to the impactor. The aerosol particles were collected on disks of uncoated aluminium as an organic coating might have lead to the adsorption of vapor phase substances. For information on the size fractionation of the atmospheric particles by the cascade impactor see Table 1. The flow through the impactor was set at 8.2 m³ h⁻¹ (0 °C, 1013 mbar) by a critical nozzle. The particle load was obtained from the difference between the filter and the aluminium disk weights before and after sampling. They were equilibrated for 24 hours in a dessicator using silicagel prior to weighing. For the determination of the substances' distribution the impactor stages and backup filter were each analyzed separately. In the coarse particle fractions only small substance amounts were expected. For this reason the particles of the two upper impactor stages (aerodynamic diameters $\geq$ 4.05 μm) were analysed together. Therefore, five particle and one XAD fractions were analyzed for each sampling period.

A cocktail of ¹³C-labeled substances was added to each fraction before the extraction. The fractions were extracted ultrasonically three times with hexane/acetone (v:v;1:1) for 10 minutes. The three extracts of each fraction were combined and dried over Na_2SO_4. Raw extracts were evaporated to a volume of about 1 ml. Sample cleanup was done by column chromatography: A glass column (10 mm i.d.) was packed with 5 g silica gel and 3 g neutral alumina (Brockmann activity 5). After application of the extract the substances were eluted with 50 ml hexane/diethyl ether (v:v;20:1). After evaporation to a volume of 1 ml the samples were transferred to 100 μl vials, evaporated under a stream of purified nitrogen and the final volume adjusted to 25 μl with toluene.

GC/MS-quantification was performed on a Hewlett Packard GC 5890 / MSD 5970 using a Hewlett Packard Ultra 2 column. The carrier gas was helium. The injector and interface temperatures were 280 °C. The GC temperature program was as follows: 100 °C - 1 min, 10 °/min to 300 °C, 9 min isotherm.

Results and Discussion

Concentrations and Size Distribution of the Atmospheric Particles

The particle concentrations in the atmosphere ranged between 10.9 and 38.1 μg m⁻³ during the six sampling intervals. A typical size distribution is shown in Fig. 1. At the normally relative low particle concentrations the portion of particles with aerodynamic diameters of $\leq$ 1.35 μm was always about 70 %.
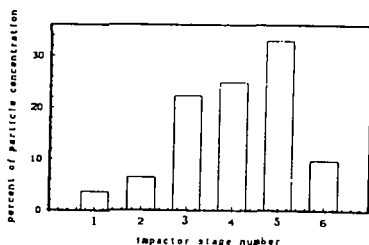

Fig. 1

Typical Size Distribution of the Atmospheric Particulate Matter

(For information on the particle size fractions see Table 1)

Organohalogen Compounds 1

Concentrations and Particle Bound Portion of the Analyzed Substances

The total substance concentrations (vapor phase + particles) and the particle bound portions are listed in Table 2.

Table 2: Concentrations and Particle Bound Portions of the investigated chemicals

Substance	Concentration (Vapor Phase + Particles) pg m^{-3}	Particle Bound Fraction %
PCB 101	5.6 - 11	n.d. - 13
PCB 153	4.1 - 11	n.d. - 47
p,p'-DDE	6.2 - 11	18 - 41
p,p'-DDT	24 - 74	73 - 88
BaP	1200 - 3400	100
BghiP	1500 - 3000	100

At ambient temperatures between -5.9 and 1.8 °C neither BghiP nor BaP were detected in the vapor phase. The particle bound portions of p,p'-DDT and p,p'-DDE amounted to 32-88 and 18-41 % respectively. For the two PCBs particle bound portions were found from not detected - 25 % (PCB 101) and not detected - 47 % (PCB 153).

The low overall concentrations and small particle bound fractions of the organochlorine compounds, especially for the PCBs, lead to analytical difficulties. Because of the separate analysis of the different particle size ranges, the substance amounts often did not exceed the detection limits (see Table 3).

Table 3: Detection Limits

Note: Detection limits are not fixed values, since they depend on a series of parameters like sample matrix, condition of the GC-column and precolumn, and sample cleanup. Detection limits were evaluated for every sample. Therefore, ranges are given.

Substance	Amount in Sample (ng) range (mean)	Injected Amount (ng) range (mean)	Atmospheric Concentration (pg m^{-3}) range (mean)
PCB 101	0.2 - 0.77 (0.4)	8 - 31 (16)	0.4 - 1 (0.7)
PCB 153	0.2 - 1.2 (0.7)	8 - 48 (28)	0.4 - 3.1 (1.4)
p,p'-DDE	0.3 - 1.3 (0.6)	12 - 52 (24)	0.6 - 5 (1.9)
p,p'-DDT	0.5 - 10 (2.7)	20 - 400 (108)	1.3 - 23 (6.2)
BaP	≈ 2.4	≈ 100	≈ 6
BghiP	≈ 2.7	≈ 110	≈ 7

Substance Distribution with Respect to Particle Size

The distribution of the investigated substances is presented in the Figures 2 - 6.
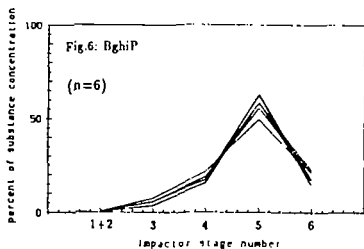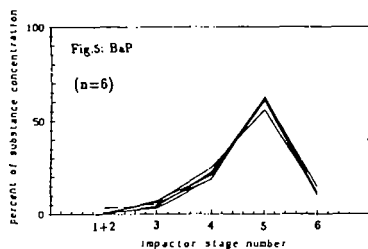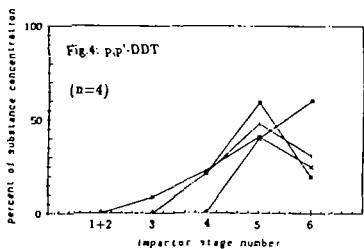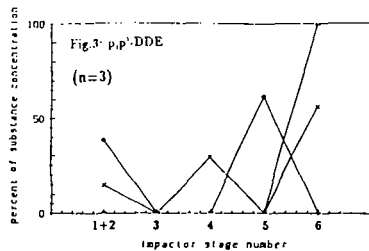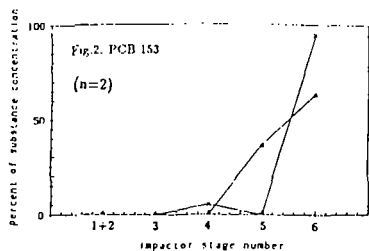
Figures 2 - 6
Size Distribution of the
investigated substances
(n represents the number of samples
in which the substance could be
detected on the particulate matter)

Table 1:   Characteristics of the Cascade Impactor

stage	Cut-Off Diameter μm	Mean Diameter μm	Hole Diameter mm
1	12.2	-	
2	4.05	7.0	4.0
3	1.35	2.3	1.3
4	0.45	0.78	0.5
5	0.15	0.26	0.3
6 (backup filter)	≤ 0.15		

The PAHs and p,p'-DDT show distributions of high reproducibility. Maximum concentrations always were found on particles of $\leq 0.45\ \mu m$. PCB 153 could be quantified on the particulate matter in two cases. This substance also occurred nearly exclusively on particles of the impactor stage 5 and the backup filter corresponding to particle diameters of $\leq 0.45\ \mu m$. We do not show the results for PCB 101, for it could be quantified on the particulate matter in only one case. There the maximum concentration ($\geq 80\ \%$) was found on particles with diameters of $\leq 0.15\ \mu m$. The distribution of p,p'-DDE was less uniform than for the other substances. Still about 70 % of the particle bound fraction were quantified on particles with diameters $\leq 1.35\ \mu m$.

It can be concluded that the particle bound portions of all these substances in the atmosphere are concentrated on accumulation mode particles. These particles comprise about 70 % of the mass and most of the surface area of atmospheric particulate matter and have long atmospheric residence times. Therefore pollutants adsorbed on these particles will be transported over long distances leading to a deposition even in background regions.

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